

## Micro – ESCA/NEXAFS at Beamline 6.3.2

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### INTRODUCTION

We have developed a micro-ESCA/NEXAFS end station for CXRO beam line 6.3.2 at the ALS. Initial experiments were performed in the total yield mode for micro-NEXAFS. The beam line 6.3.2 allows tunability of the EUV/soft x-ray energy between 50 –1300 eV region with high spectral resolution, high flux and accurate wavelength/energy calibration. The system achieves a spatial resolution approaching 1  $\mu\text{m}$  coupled with the chemical specificity of the NEXAFS technique. This high spatial resolution was achieved using an x-ray microfocusing system based on a Kirkpatrick-Baez mirror optical system made by elastically bending a pair of side profiled silicon mirrors. Samples are mounted on an X-Y stage, which allows 2D micro-ESCA/NEXAFS images of samples to be obtained by scanning, with sub- $\mu\text{m}$  precision. Some representative results are presented.

### BACKGROUND - ESCA ANALYSIS

Electron Spectroscopy for Chemical Analysis (ESCA) is a widely-used analytical technique for investigating the chemical composition of solid surfaces. The technique is a basic tool in a wide variety of materials science related fields such as metallurgy, corrosion, contamination, tribology, plastics, polymers and ceramics, and is proving useful in geochemistry, environmental sciences, and in fact in any field in which requires chemical analysis of a surface that can be maintained in ultra-high vacuum. Surface analysis by ESCA is accomplished by illuminating the solid, under UHV conditions, with soft x-rays of a single energy. The spectrum of the emitted photoelectrons is then analyzed with an appropriate electron spectrometer. Since the mean free path of the electrons is very small, the detected electrons originate from the topmost few atomic layers (20-30 Å); hence ESCA is a *surface*, rather than a *bulk*, analysis technique although greater depths can be investigated through ion etching. Each element has a unique photoemission spectrum, and the spectrum of a mixture or compound of elements is approximately the sum of the spectral peaks from the individual elements. Quantitative data can be obtained from the peak heights (or areas) and identification of the chemical states (e.g. valence) can be made from the exact peak positions and spectral line shapes. This information allows the identification of functional groups and molecular types. For example, ESCA can readily distinguish between the ionic and covalent forms of fluorine. For most metals, ESCA can distinguish between oxidized and reduced species. ESCA is sensitive to as low as 0.1 atom percent and detects elements except H and He. It can be applied to all solid materials, including insulators such as polymers and glasses. With the addition of auxiliary sample preparation facilities the technique becomes more powerful. For example an ion gun for sputtering enables compositional depth profiling to be carried out to sub-nanometer spatial resolution.

## **MICRO-ESCA WITH SYNCHROTRON RADIATION**

The lateral spatial resolution of ESCA is determined by the size of the x-ray spot on the sample. In commercial ESCA machines, this spot is produced by a more or less conventional x-ray tube (usually with an aluminum or magnesium anode to give Al K or Mg K x-rays). These spots are characteristically of the order of a few hundred  $\mu\text{m}$  to a millimeter in diameter. Hence commercial ESCA machines are incapable of resolving the microstructure of an inhomogeneous material. A number of "Small-spot ESCA" machines have been developed. These machines still employ conventional x-ray tubes, using focusing or collimating optics to achieve an x-ray spot of the order of tens of  $\mu\text{m}$ . Thus the range of lateral structures that can be investigated with commercial ESCA machines ranges from 10  $\mu\text{m}$  to 2 mm. A summary chart of Detection Limits vs. Probe Size for analytical techniques published by Charles Evans Associates shows that at 10  $\mu\text{m}$  resolution the detection limit for commercial ESCA machines is about  $10^{20}$  atoms/cc or a fraction of 1%.

It is clear that even a bending magnet source on a third generation storage ring such as the ALS is many orders of magnitude brighter than the conventional hot-cathode x-ray tubes used in commercial ESCA machines. Thus the possibility exists for improving the resolution and sensitivity by orders of magnitude. Improvement of the spatial resolution to the order of 1  $\mu\text{m}$  would enable chemical mapping on a scale appropriate to the study of grain boundaries of alloys, ceramics, rocks or minerals, of corrosion-induced cracks, wear tracks in bearings or on magnetic recording media, contamination of optical surfaces...etc. In addition the higher brightness of the ALS should allow the lowering of the detectivity limit by an order of magnitude to the order of 0.1%, thus allowing the study of subtle phenomena.

### **MICRO-ESCA/NEXAFS AT BEAMLINE 6.3.2**

NEXAFS (Near-Edge X-ray Absorption Fine Structure) spectroscopy is another spectroscopic method for determining the electronic and structural properties of molecules in solid state systems. The "total yield" method, in which the electron current from the sample is measured directly (as the sample drain current) or with an auxiliary electron detector such as a channeltron is simple to implement. An advantage of the NEXAFS over the ESCA technique is that it does not require ultra-high vacuum. The high flux, high spectral resolution, accurate energy calibration, and ease of use have made beamline 6.3.2 popular for NEXAFS spectroscopy. A wide range of measurements primarily using the total yield technique, have been carried out on the beamline since its commissioning in 1995. It soon became evident that reduction of the x-ray spot size to  $\sim 1 \mu\text{m}$  would have the same advantages for the NEXAFS technique as for ESCA, i.e. would allow solid state chemical analysis to be performed at microstructural scales.

On beamline 6.3.2, this small x-ray spot is obtained by using a Kirkpatrick-Baez (K-B) optical system to demagnify a pinhole positioned at the center of the reflectometer chamber. The desired elliptical figure of the K-B optics is obtained elastic bending of profiled mirrors bent with unequal end couples. This technique has been developed and refined by CXRO personnel over the course of many years [1,2] to the point where spot sizes of  $\sim 1 \mu\text{m}$  are routinely achieved [3].

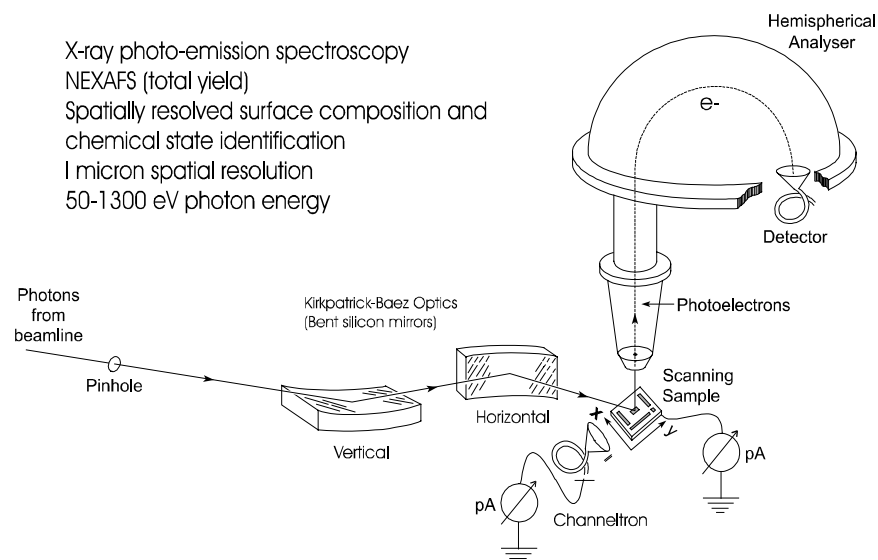


Figure 1. Schematic of micro-ESCA/NEXAFS end station as installed on beamline 6.3.2

The layout of the of the micro-ESCA/NEXAFS end station is shown in Figure 1. A new UHV tank and stand was built to house the a refurbished SPECS EA 10 plus analyzer, the sputtering gun from a Leybold-Heraeus ESCA system (both obtained from another DoE laboratory on surplus) and a vacuum new transfer stage. This tank also houses the K-B optical, system including a visible alignment and focusing microscope. The sample puck is carried on a scanning x-y stage designed and built by CXRO personnel. The scanning and data acquisition are controlled by the same LABVIEW software that runs the 6.3.2 beamline. The system has been installed on beamline 6.3.2 several times and has been fully exercised (except as noted below). A spot size in the range of 1-2  $\mu\text{m}$  has been demonstrated with the mirror system and the scanning stage has been shown capable of sub-micron accuracy.

## RESULTS

A wide variety of samples has been scanned and some representative results are shown below. Figure 2. shows the visualization of standing waves on the surface of a Mo/Be multilayer reflector. The lozenge shape outlines a crater in the surface of the multilayer produced by sputter etching. The fringes around the border represent contours of photoelectron emission intensity obtained by scanning the surface of the multilayer with the monochromator wavelength set at the Bragg peak, approximately 11.5 nm. These variations map the intersections of the nodes and antinodes of the multilayer standing wave with the sloping sides of the sputter crater.

Figure 3 is a scan of a sample of the hexagonal form of boron nitride (hBN) deposited on a silicon wafer. By treatment with an ion beam, the region at the left of the frame has been partially converted to the cubic form of BN. The scan was made with the monochromator tuned to the  $\pi^*$  resonance of hBN at 191.8 eV. This resonance disappears in cubic BN; thus the areas that have been converted to cubic BN appear darker. In this scan one can clearly see the microstructure, including cracking, of the cubic BN region.

### Sputter crater in Mo/Be multilayer

Figure 2. Visualization of standing waves on the surface of a Mo/Be multilayer reflector at a wavelength of 11.5 nm. The fringes surrounding the "lozenge" shape represent regions of high and low photoelectron emission resulting from the intersection of the standing wave in the multilayer with the sloping edges of the crater.

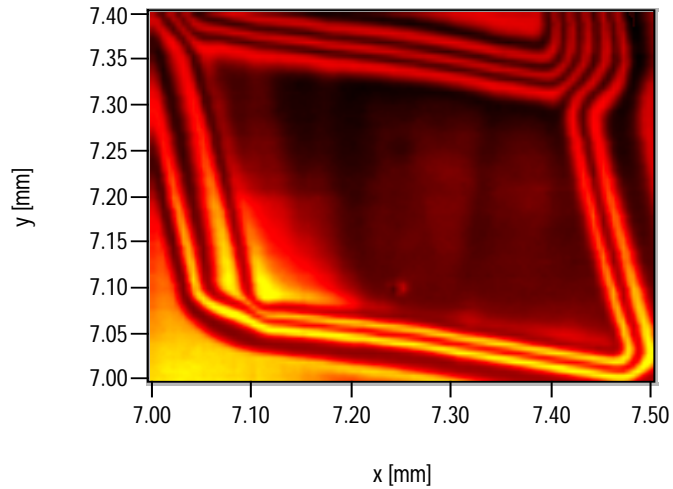
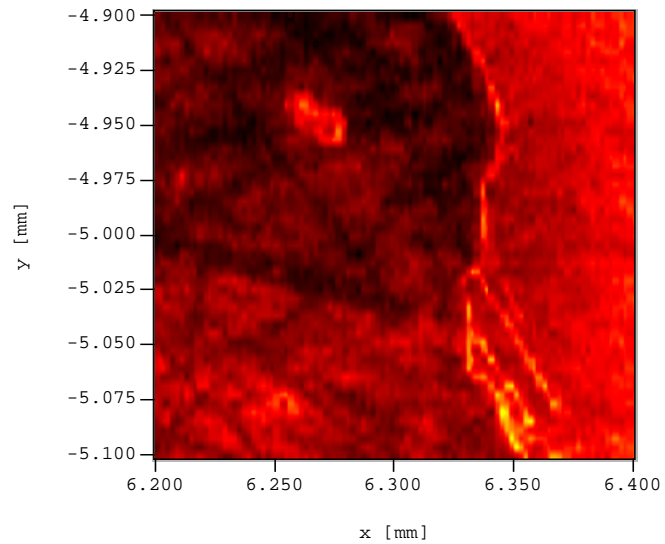


Figure 3. High resolution scan of an hBN film deposited on a silicon wafer. The region at the left of the frame has been partially converted to the cubic form of BN. The scan was made at the energy of the  $\pi^*$  resonance of hBN, which disappears in the cubic form. Hence the region at the left appears darker. (Sample provided courtesy of L. Terminello, LLNL).



## REFERENCES

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